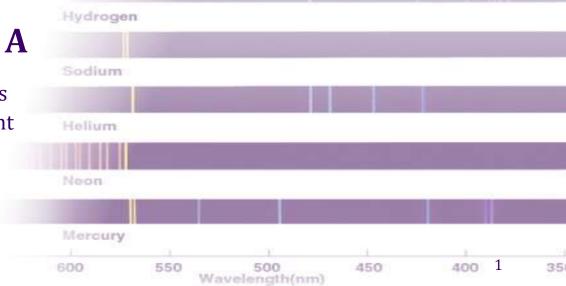


Photonics

R. Baets / E. Bente

Photons and Atoms Part A

Introduction quantum mechanics concepts
Atoms, molecules and interaction with light
Thermal light
Luminescence light



Photons and atoms

Generation/absorption of light ⇒ interaction of light with matter

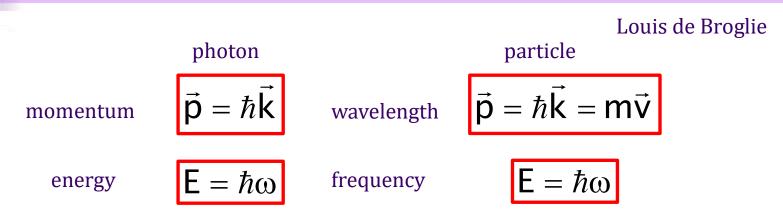
- Matter= atoms
 - isolated (noble gas, gas vapour)
 - interacting (molecules,fluid, solid)

Structure of atoms

Interaction electromagnetic waves - atoms
described by quantum mechanics
(Quantum mechanics was discovered by studying this subject)

Light mainly interacts with the outer (valence) electrons in atoms/molecules/solid these electrons absorb or emit the energy

Particles as waves

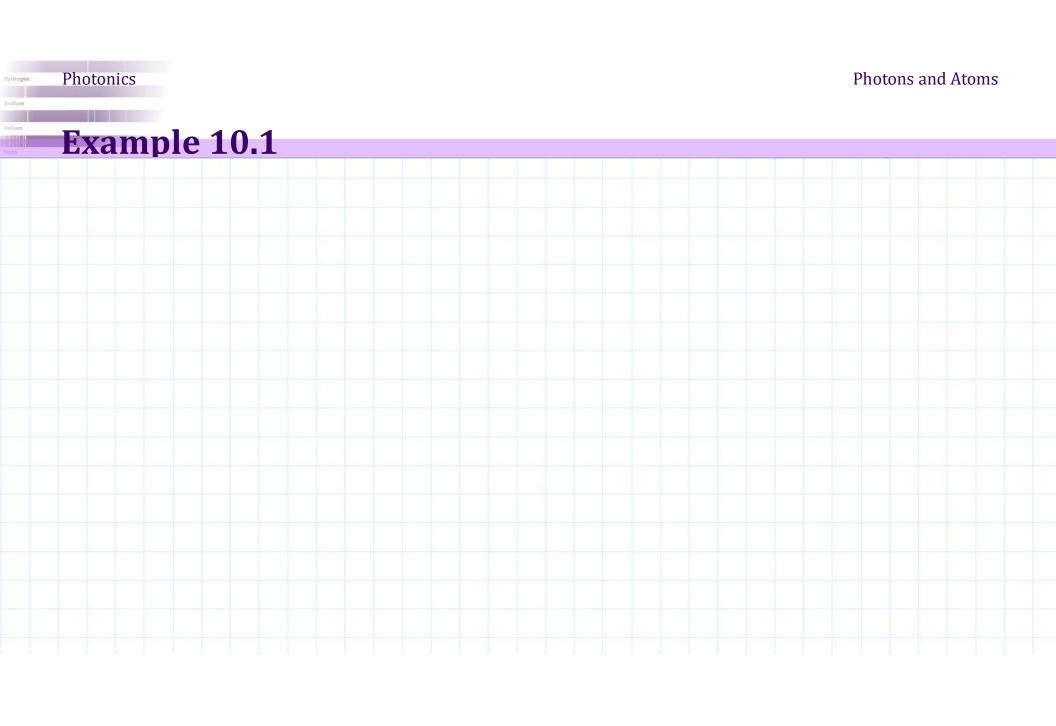


Assign a wavelength and frequency to a particle

probability finding a <u>photon</u>
proportional to
amplitude electric field squared
(= power)

electric field is solution of the classical wave equation probability finding a <u>particle</u>
proportional to
amplitude wave function squared

wave function is solution of the Schrödinger equation



Photonics

Photons and Atoms

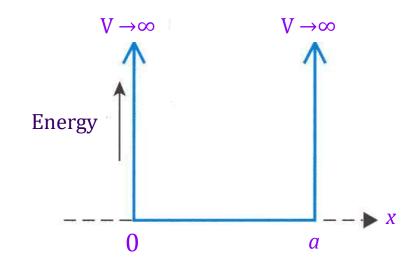
Particle in an infinite potential well 1dim

Particle mass *m*

Potential energy V(x) (time independent)

$$V(x) = 0 \text{ for } 0 < x < a$$

$$V(x) \rightarrow \infty$$
 for $x \le 0$ and $x \ge a$



This is a **bound** system

The particle (e.g. electron) cannot be outside 0 < x < a

The particle has only kinetic energy

$$E_{kin} = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} = \frac{h^2}{\lambda^2 2m}$$

Particle in an infinite potential well 1dim

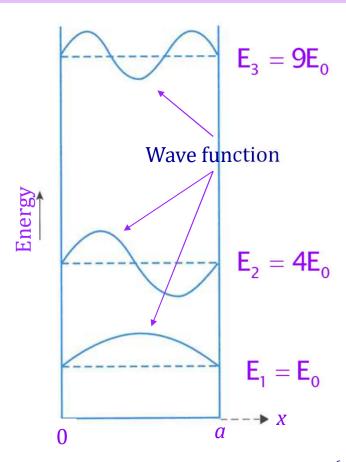
Solution: Particle wavelength has to fit in the potential well like a standing wave in a resonator

$$n\frac{\lambda}{2} = a$$
 $n = 1, 2, 3....$

$$E_n = \frac{p^2}{2m} = \frac{h^2}{\lambda^2 2m} = E_0 n^2$$
 $E_0 \equiv \frac{\hbar^2 \pi^2}{2ma^2}$

Bound system:

- Energy <u>quantization</u> (counting states)
- States identified by *n*: quantum number)
- Lowest energy (ground state) $E_0 > 0$
- Values of the energy level depend on V(x)





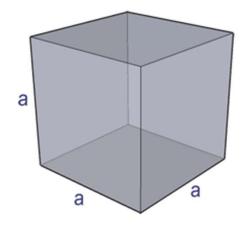
Particle in 3D potential well (a cube)

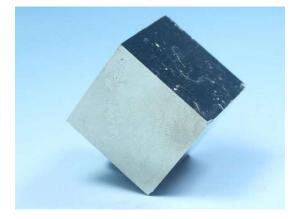
Solutions are like EM plane waves in a 3D resonator

Energy levels of particle

$$E_{n_1,n_2,n_3} = E_0 (n_1^2 + n_2^2 + n_3^2) E_0 \equiv \frac{\hbar^2 \pi^2}{2ma^2}$$

Three quantum numbers n_1 , n_2 , n_3 , characterise each state in 3D well one quantum number per degree of freedom





https://m.dhgate.com/product/the-cube-natural-mineral-crystal-natural/373597893.html

Quantum states - energy levels

Each quantum <u>state</u> of a system is characterized by its set of quantum numbers. One quantum number per degree of freedom of the system E.g. (n_1, n_2, n_3)

Each state of a system means that it has a specific energy, we call this: the energy level of the system.

Multiple states of the system (multiple sets of quantum numbers) can have the same energy (energy levels).

The values of energies of the system in the different states depend on the specifics of the system (potential energy of particle as a function of its position)

Density of states 3D potential well (cube)

If the cube becomes large ($a \gg \lambda$ electron) (e.g. several cm³) E_0 becomes very small (but still discrete energy states)

In practice we then don't count the individual states any more but:

Use the concept of density of states: g(E)

If N is the number of states at energy E in an interval ΔE

$$N \approx g(E) \cdot \Delta E$$

For the 3D potential well (cube) the density of states is

$$g(E) = C\sqrt{E}$$
 $C = \frac{\pi}{2E_0^{3/2}} = \frac{a^3(2m)^{3/2}}{2\hbar^3\pi^2} = Volume \cdot \frac{(2m)^{3/2}}{2\hbar^3\pi^2}$

Density of states per unit volume is independent of size or shape!

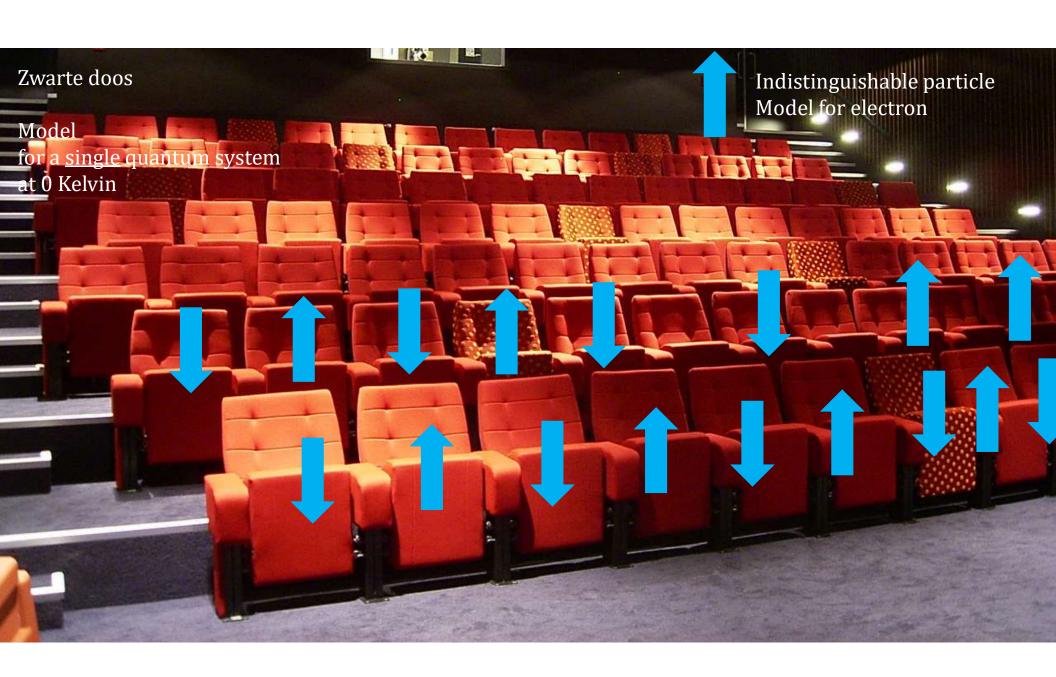
Pauli exclusion principle

- Atoms, molecules and solid state crystal: electron occupy states.
- Question:
 - How many electrons in each state within one quantum system?

Pauli exclusion principle:

no two identical particles (of the category fermions) can be in the same state of a quantum system

each state can be occupied by only two electrons
 (one with spin up, spin down)
 this makes each energy state is actually two states with (nearly) the same energy



Energy levels of atoms

- Atom is a spherically symmetric system → potential energy of electron V(r) only depends on r
- **Hydrogen atom** has simple structure of the energy levels:

$$E_n = -\frac{m_r e^4}{2\hbar^2 n^2} = E_1 \frac{1}{n^2}$$
 $n = 1,2,3,...$

- \bullet m_r is the reduced mass of the system.
- e is the elementary charge.

$$m_r = \frac{m_e \cdot M_N}{m_e + M_N} \approx m_e \quad (m_e \ll M_N)$$

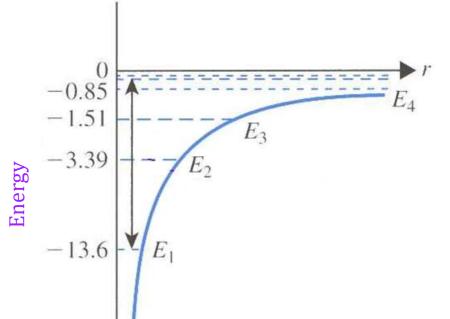
Energy difference between lower states in the order of several eV.
 → visible light

Hydrogen atom - electronic states

$$E_n = -\frac{m_r e^4}{2\hbar^2 n^2} = E_1 \frac{1}{n^2}$$
 $n = 1,2,3,...$

$$n = 1,2,3,...$$

$$E_1 = -13.6 \, eV$$



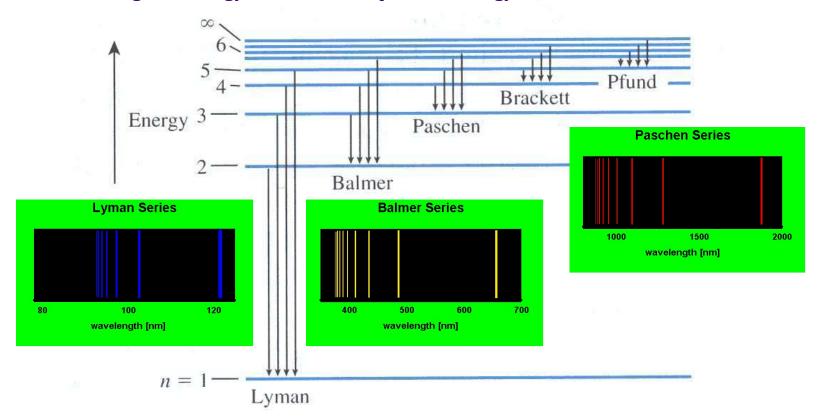
- Finite potential well Coulomb attraction
- Infinite number of states
- Distances between lower levels several 0.1 eV -10eV interaction with photons in the NIR, VIS, UV ranges
- Not all transitions allowed

Heavier atoms have a more complex energy state diagram

Photonics

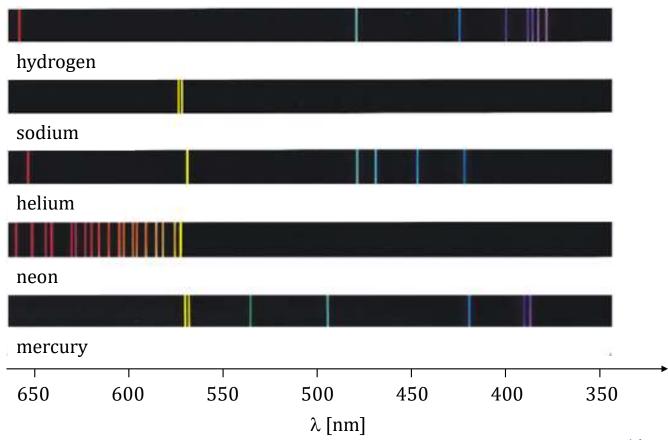
Hydrogen emission lines

Transitions: change in energy in the atom = photon energy



Spectral lines

- Every atom
 - Different energy levels
 - Fingerprint of atom



Energy levels in molecules

(mutiple atoms in one quantum system)

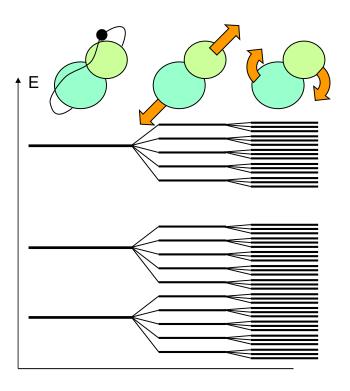
- **Electronic** states
 - Spacing: 1-10 eV
- Vibrational states
 - Atoms are vibratingHarmonic oscillator

$$E_{\nu} = \left(\nu + \frac{1}{2}\right)\hbar\omega_{res}$$
 $\nu = 1,2,3,...$ $\omega_{res} = \sqrt{\frac{k_s}{m_r}}$

- Spacing: 0.05-0.5eV
- Rotational states
 - Molecule rotating around axis

$$E_r = r(r + \frac{1}{2})\frac{\hbar}{2I}$$
 $r = 1,2,3,...$ $I = inertia$

- Spacing: 0.001-0.01eV
- Not all transitions are allowed

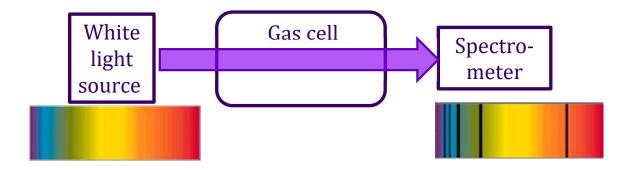


Electronic levels

Molecular vibrations

Molecular rotations

Boltzman statistical distribution



Observation: Absorption by molecules from states above ground state.

Question: Which atoms or molecules are in a state at energy E_n in equilibrium at a specific temperature T?

Boltzmann distribution (classical) describes:

for a group of atoms or molecules that are separate systems (identical but distinguisable particles)

the probability of finding an atom or molecule in a particular state at a particular temperature.

Boltzmann distribution

- Gas (no interaction) of identical atoms: Probability an atom
- is occupying level E_m

$$P(E_m) = Ae^{-\frac{E_m}{k_B T}}$$

- \mathbf{k}_{B} = Boltzmann constant
- A = constant such that:

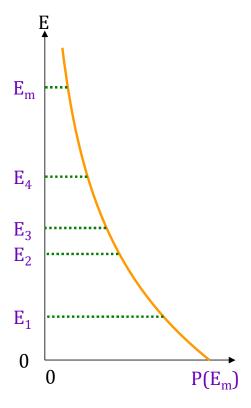
$$\sum_{m} P(E_m) = 1$$

- At temperature T in thermal equilibrium
- many (N) atoms, #atoms in state at E_m : $N_m = ANe^{-\frac{E_m}{k_BT}}$
- Population ratio:

$$\frac{N_i}{N_j} = \frac{g_i}{g_j} e^{-\frac{E_i - E_j}{k_B T}}$$

with degeneracy g_i and g_j .

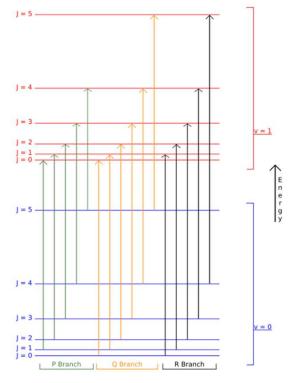
$$E_1 < E_2 < E_3 < E_4 < ... < E_m$$

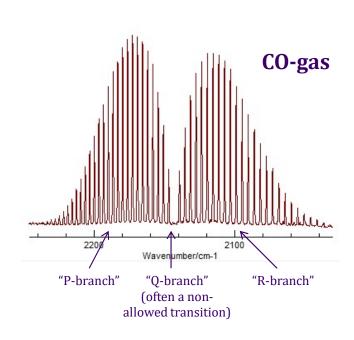


Rotational absorption spectrum

Every vibrational transition consist of a fine structure of transitions between different

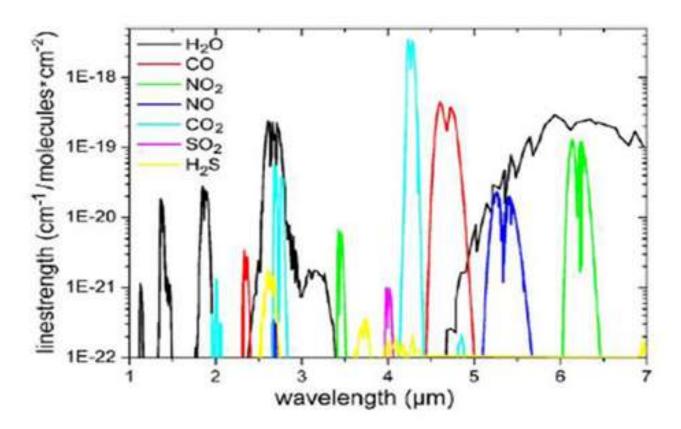
rotational states





Vibrational absorption spectrum

Infrared absorption lines caused by vibrational transitions form fingerprint



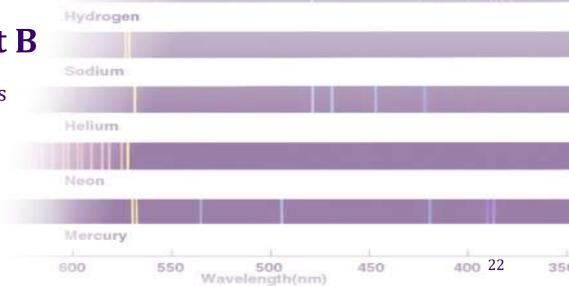


Photonics

R. Baets / E. Bente

Photons and Atoms Part B

Atoms, molecules, solid state energy levels Interaction with light

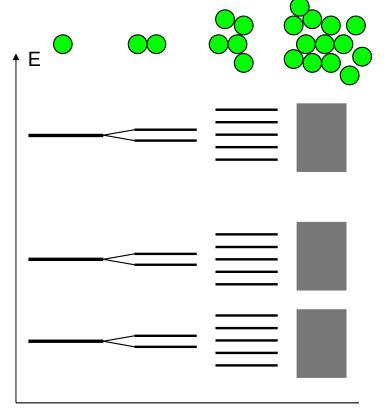


Solid state: multiple atoms

- System of N closely packed atoms $(10^{23} \text{ atoms/cm}^3)$
- Energy levels:
 - Valence electrons
 - Rotations, Vibrations
 - Splitting of each level into N energy levels



Formation of energy bands if N is very large

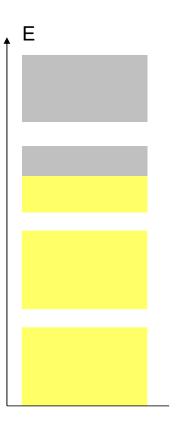


Band occupation: Metals

- Occupation of energy levels (bands)
 - Pauli: each level contains max 2 electrons
 - n electrons per atom
- single occupied levels:
 upper band (=valence band) half filled: electrons
 can easily be excited from one level to another
 - thermal
 - by applying an electric field
 - · ...



Good conduction: metals



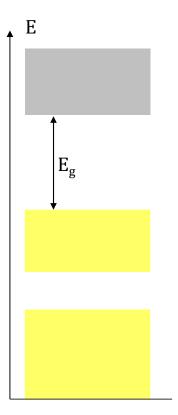
Band occupation: Isolator

- Occupation of energy levels (or bands)
 - Pauli: each level has max 2 electrons
 - n electrons per atom
- double occupied levels:
 Valence band completely filled

If the distance E_g (= "Band Gap") is large: No excitation of electrons possible



No conduction: ISOLATOR

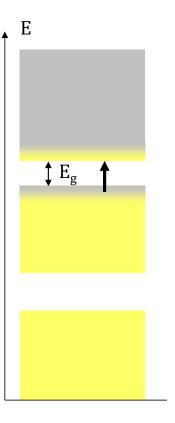


Band occupation: Semiconductor

- Occupation of energy levels (or bands)
 - Pauli: each level has max 2 electroncs
 - n electrons per atom
- double occupied levels:Valence band completely filled
- When the distance E_g (= "Band Gap") small:
 Some electrons can be excited to the conduction band where they can move freely
 - Thermal excitation
 - Excitation through electric field
 - **.**..



Some conduction: Semiconductor



Statistics electrons over states in a solid

Question: What is the probability to find an in electron in an energy state at energy E?

- Electrons in solid state:
 the electrons are fermions and follow the Pauli exclusion principle
 they have a strong interaction and form a single quantum system
 the electrons are indistinguishable
- The electrons therefore do not distribute themselves over the states according to the Boltzmann distribution. That distribution allows more than one electron in each state.
- The electrons distribute themselves over the states according to the

Fermi-Dirac distribution.

Fermi-Dirac distribution

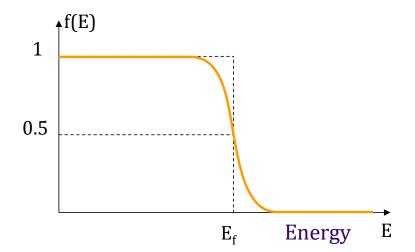
- Electrons in solid state: indistinguishable particles in a system
- Probability of the occupation of an energy level E:

$$f(E) = \frac{1}{e^{\frac{E-E_f}{k_BT}} + 1}$$
 where E_f is the Fermi-energy $f(E_f) = 0.5$

• For $E \gg E_f$:

$$f(E) \approx e^{-\frac{E - E_f}{k_B T}}$$

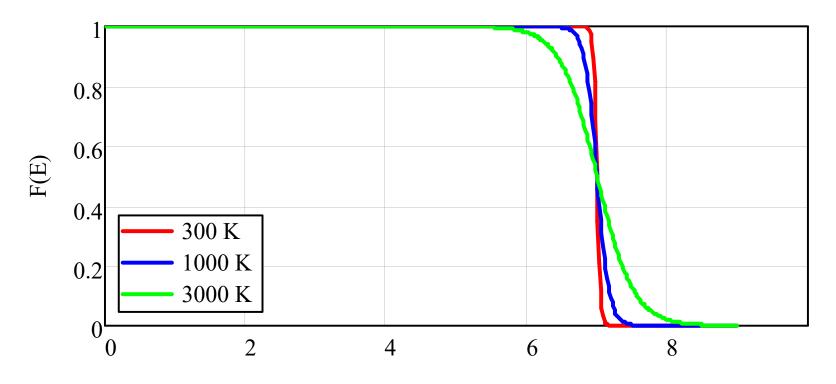
(Boltzmann approximation)



Example Fermi function

 k_B^{450} T = 0.0259 eV at T = 300K

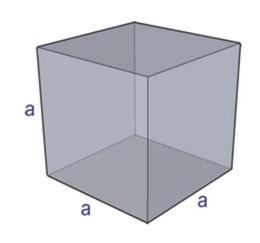
$$E_{\rm f} = 7.0 \; {\rm eV}$$

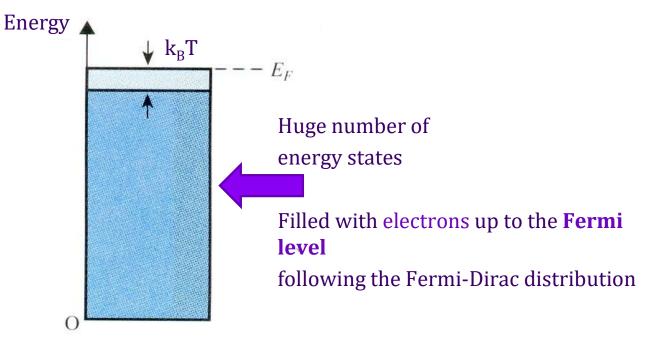


Energy in eV

3D potential well -model for a metal

Macroscopic block of metal e.g. a = 1cm



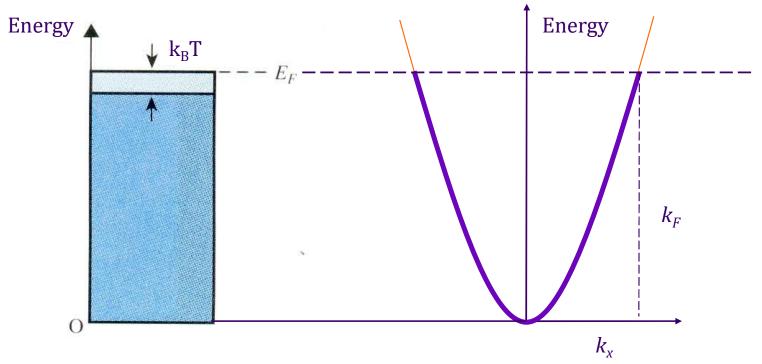


- Density of electrons at energy *E*: N(E)dE = g(E)f(E)dE
- Such a model will be used in Chapters 14 and 15

3D potential well - E-k relation

All electron energy is kinetic energy

$$E = E_{kin} = \frac{p^2}{2m} = \frac{\hbar^2}{2m}k^2$$



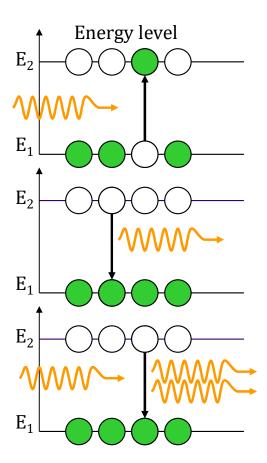
Such a model will be used in Chapters 14 and 15

Interaction between matter and light

- Basic processes two-energy level systems
- Relation between those processes

Emission and absorption

- Transition between atomic or molecular levels: emission or absorption of a photon
- Absorption:
 - Photon hits the system
 - System brought into excited state
- Spontaneous emission:
 - System goes back to lower state
 - Emission of photon
- Stimulated emission
 - Photon hits system
 - System goes back to lower state
 - Emission of identical photon



Einstein description

Probability (per s) that an atom absorbs one photon from a specific EM mode and thereby goes to an excited state (p_{abs})

=

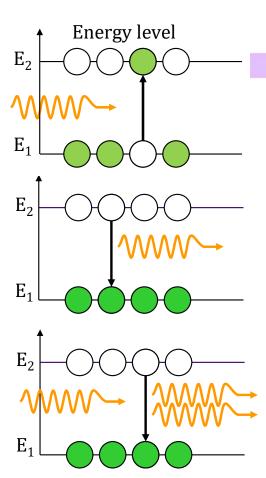
• Probability (per s) that an atom spontaneously decays with the generation of <u>one photon</u> in a <u>specific EM mode</u> (p_{sp})

=

• Probability (per s) that an atom falls back to the ground state under the influence of <u>one photon</u> in a <u>specific EM mode</u> (p_{st})

$$p_{sp} = p_{abs} = p_{st} \equiv \frac{c}{V} \sigma(v)$$
Cavity volume

transition cross-section



34

Spontaneous emission

 Probability of transition with spontaneous emission of one photon in one mode of cavity with volume V

$$p_{sp} = \frac{c}{V}\sigma(v)$$

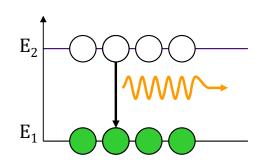
• With $\sigma(v)$ a function centered around

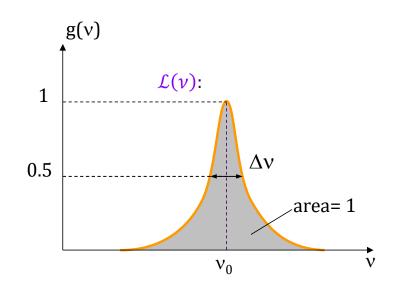
$$v_0 = \frac{E_2 - E_1}{h}$$
Planck's constant
6.626e-34 J·s

• After normalization: line shape function $\mathcal{L}(\nu)$:

$$\mathcal{L}(\nu) = \frac{\sigma(\nu)}{\int \sigma(\nu) d\nu}$$

with 'linewidth' $\Delta \nu$. (Typically $\Delta \nu \ll \nu_0$)

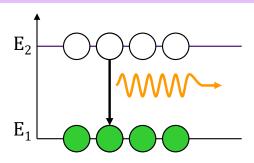




Spontaneous emission

Density of EM modes in a cavity(= # EM modes in the cavity / volume freq.)

$$M(\nu) = \frac{8\pi\nu^2}{c^3} = \frac{8\pi}{\lambda^2 c}$$



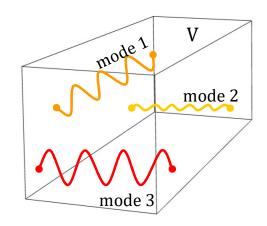
Total emission probability of photon:

$$P_{Sp} = \int p_{Sp} V M(\nu) d\nu = c \int \sigma(\nu) M(\nu) d\nu \approx c M(\nu_0) \int \sigma(\nu) d\nu$$

$$p_{Sp} = \frac{c}{V} \sigma(\nu)$$
M constant over lineshape
$$P_{Sp} \approx \frac{8\pi}{\lambda_0^2} \int \sigma(\nu) d\nu$$

= "A-coefficient of Einstein" A_{21} (independent of cavity volume V)

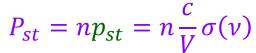
Spontaneous lifetime: $au_{Sp} = \frac{1}{P_{Sp}} = \frac{1}{A_{21}}$



Stimulated emission

- **Emission of an IDENTICAL photon** triggered by an incident photon (basis of laser operation) → interaction with only one mode
- Probability for a transition with stimulated emission in a cavity with volume V:

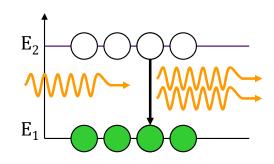
$$P_{st} = np_{st} = n\frac{c}{V}\sigma(v)$$



with n the number of photons already present in that mode

Total emission (stimulated plus spontaneous) probability:

$$p_{sp} + P_{st} = (n+1)\frac{c}{V}\sigma(v)$$
 zero point energy of a mode extra photons



Stimulated emission

$$P_{st} = np_{st} = n\frac{c}{V}\sigma(v)$$

Interpretation:

- n c/V is the FLUX DENSITY of the number of photons
 (i.e. the number of incident photons per s and m²)
- $\sigma(v)$ is the cross section in m² for stimulated emission
- The product is the probability (per s) that stimulated emission occurs

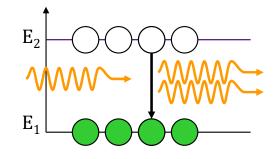
Stimulated emission

Cavity with spectral energy density $\rho(v)$ (per volume, per frequency).

photons in[
$$\nu$$
, ν + $d\nu$] in cavity

$$\frac{\rho(\nu)}{h\nu}Vd\nu$$

$$P_{st} = \int p_{st}(\nu) \frac{\rho(\nu)}{h\nu} V d\nu = c \int \frac{\rho(\nu)}{h\nu} \sigma(\nu) d\nu$$



$$\begin{array}{l} \begin{array}{l} \rho \text{ const over} \\ \text{lineshape} \end{array} \approx c \frac{\rho(\nu_0)\lambda_0}{h} \int \sigma(\nu) d\nu = \frac{\lambda_0^3}{8\pi h \tau_{sp}} \frac{\rho(\nu_0)}{P_{sp}} \\ = \frac{\bar{n}}{\tau_{sp}} = B_{21} \rho(\nu_0) \end{array}$$

- with $\bar{n} = \frac{\lambda_0^3}{8\pi h} \rho(\nu_0)$ the average number of photons per mode $M(\nu) = \frac{8\pi \nu^2}{c^3} = \frac{8\pi}{\lambda^2 c}$

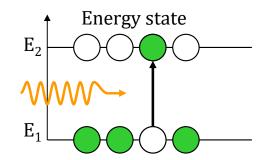
With
$$B_{21}$$
 the "Einstein B-coëfficient".
$$B_{21} = \frac{\lambda_0^3}{8\pi h \tau_{sp}} = \frac{\lambda_0^3 A_{21}}{8\pi h}$$

$$M(\nu) = \frac{8\pi\nu^2}{c^3} = \frac{8\pi}{\lambda^2 c}$$

Absorption

Probability of a transition due to absorption in a cavity with volume V:

$$P_{abs} = np_{abs} = n\frac{c}{V}\sigma(v)$$



With n the number of photons present in the mode

$$\begin{aligned} P_{abs} &= P_{st} \\ &= \frac{\bar{n}}{\tau_{sp}} = B_{12} \, \rho(\nu_0) \\ &= \bar{n} P_{sp} \end{aligned}$$

$$B_{12} = B_{21}$$

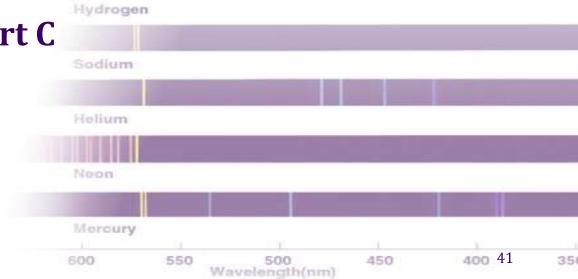


Photonics

R. Baets / E. Bente

Photons and Atoms - Part C

Thermal light Luminescence light



Thermal light

- Two-level atoms in thermal equilibrium with a cavity
- Black body radiation

Thermal equilibrium

- Atoms, molecules of solids,... in thermal equilibrium: emission and absorption of photons
- Cavity with V=1, walls with many atoms per volume unit
 - \blacksquare N₁ atoms in state E₁.
 - N₂ atoms in state $E_2 > E_1$.
 - \overline{n} photons in every EM-mode within linewidth of $\mathcal{L}(v)$:

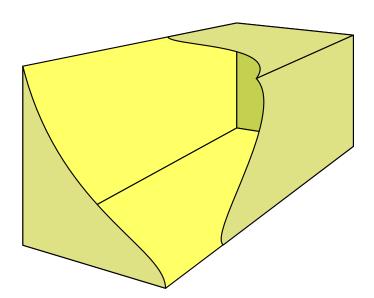
$$P_{abs} = P_{st} \frac{\bar{n}}{\tau_{sp}}$$

Thermal equilibrium:

$$\#(E_1 => E_2) = \#(E_2 => E_1)$$



absorption = stimulated+ spontaneous emission



Equilibrium between material and photons

- Spontaneous emission
 - Proportional to N_2

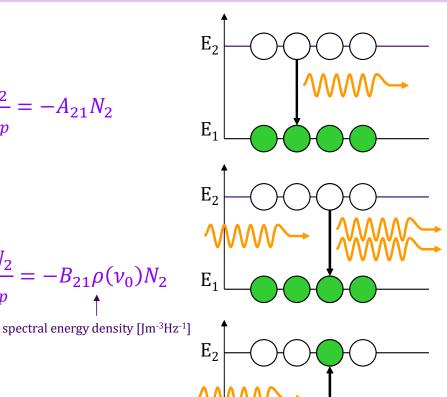
$$\left. \frac{dN_2}{dt} \right|_{sp} = -\frac{dN_1}{dt} \Big|_{sp} = -N_2 P_{sp} = -\frac{N_2}{\tau_{sp}} = -A_{21} N_2$$

- Stimulated emission
 - Proportional to N_2
 - Proportional to \bar{n}

$$\left. \frac{dN_2}{dt} \right|_{st} = -\frac{dN_1}{dt} \Big|_{st} = -N_2 P_{st} = -\frac{\bar{n}N_2}{\tau_{sp}} = -B_{21} \rho(\nu_0) N_2$$

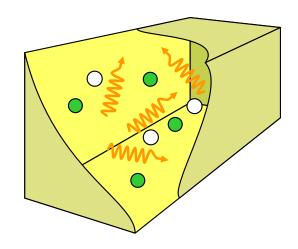
- Absorption:
 - Proportional to N_1
 - Proportional to \bar{n} (photon flux)

$$\left. \frac{dN_2}{dt} \right|_{abs} = -\frac{dN_1}{dt} \Big|_{abs} = N_1 P_{abs} = \frac{\bar{n}N_1}{\tau_{sp}} = B_{21}\rho(\nu_0)N_1$$



Discuss

A box with 2-level atoms and photons:



 \bar{n} photons in interacting mode

 N_1 ground-state atoms

 N_2 excited atoms

What fraction of atoms will be excited in thermal equilibrium?

Photonics

Photons and Atoms

Equilibrium between material and photons

Total flux:

$$\frac{dN_2}{dt} = -\frac{dN_1}{dt} = \frac{dN_2}{dt} \bigg|_{sp} + \frac{dN_2}{dt} \bigg|_{ab} + \frac{dN_2}{dt} \bigg|_{st} = \frac{1}{\tau_{sp}} (\bar{n}N_1 - N_2(\bar{n}+1))$$

Does not take into account

- Other energy levels
- Other (non-radiative) processes

• Equilibrium:
$$\frac{dN_2}{dt} = -\frac{dN_1}{dt} = 0$$
 (absorption = emission)

$$\frac{N_2}{N_1} = \frac{\bar{n}}{\bar{n}+1}$$

Equilibrium between material and photons

Equilibrium:

$$\frac{N_2}{N_1} = \frac{\bar{n}}{\bar{n}+1} \quad \longleftarrow$$

• Boltzmann distrib.:
$$\frac{N_2}{N_1} = e^{-\frac{E_2 - E_1}{k_B T}} = e^{-\frac{h\nu}{k_B T}}$$

Average number of photons with frequency v:

$$\bar{n} = \frac{1}{e^{\frac{h\nu}{k_BT}} - 1}$$

It turns out this expression is also valid for

- Multiple energy levels
- continuum

Spectrum of a blackbody radiator

Energy of a radiating mode with frequency ν:

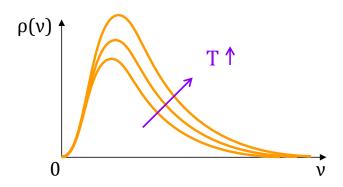
$$\bar{E} = \bar{n}h\nu = \frac{h\nu}{e^{\frac{h\nu}{k_BT}} - 1}$$

For low photon energies: $h\nu \ll k_B T$ $\overline{E} \approx k_B T$

Spectral energy density = Mode-energy x mode density

$$\rho(\nu) = M(\nu)\overline{E} = \frac{8\pi h \nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{k_BT}} - 1}$$

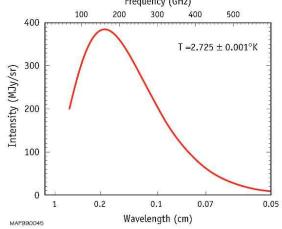
- = Black body spectrum
- A black body radiator emits an EM spectrum only characterized by its temperature.



Blackbody radiator

- A black body radiator emits a EM spectrum only characterized by its temperature.
- It is an idealized concept. Real objects radiate with lower efficiency that can be wavelength dependent (emissivity)
- But real devices/situation can be close to it.
- Sun's surface 5778 K
- Earth approximately 300K
- Background in the universe 2.725 K

SPECTRUM OF THE COSMIC MICROWAVE BACKGROUND Frequency (GHz)



https://map.gsfc.nasa.gov/universe/bb_tests_cmb.html

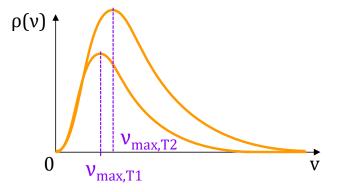
Properties of a blackbody

The most important properties only depend on temperature

Wien's law

$$v_{max} = 2.821436 \frac{k_B T}{h}$$

Law of Stephan-Boltzmannj total emitted power per unit area



$$j = \sigma T^4$$
 with $\sigma = \frac{2\pi^5 k_B^4}{15c^2 h^3} = 5.6704 \cdot 10^{-8} \frac{W}{m^2 K^4}$

Example: temperature of sun T = 5778 K

$$\rightarrow \nu_{\text{max}} = 3.378 \ 10^{14} \ \text{Hz} \Rightarrow 887.4 \ \text{nm}$$

(= where the maximum spectral energy density $\underline{per\ unit\ frequency}$ is)

https://phet.colorado.edu/en/simulation/blackbody-spectrum

Black body radiation energy density $\rho(\lambda)$

Black body radiation energy density as a function of wavelength.

$$\rho(\lambda) = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda k_B T}} - 1}$$
 Energy per unit volume, per unit of wavelength

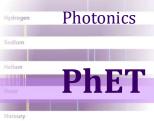
Energy per unit volume,

Wien's law in wavelength

$$\lambda_{max} = 0.0028978 \frac{1}{T} m$$

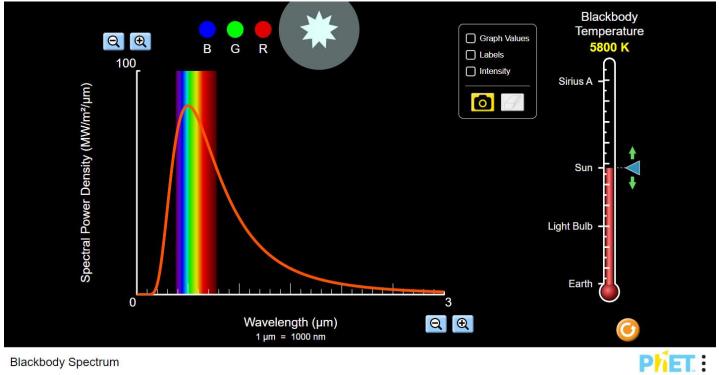
Note that
$$\lambda_{max} \neq \frac{c}{v_{max}}$$
 Since they stem from different entities!

 v_{max} as defined on previous slide: the frequency at which the spectral power density per unit of frequency is maximum



https://phet.colorado.edu/en/simulations/

https://phet.colorado.edu/sims/html/blackbody-spectrum/latest/blackbody-spectrum_en.html



Blackbody Spectrum

52

Black body radiation spectral radiance

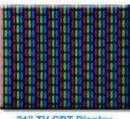
- In literature also expressions for the spectral radiance of the black body radiation are presented (without explicit mentioning)
- Spectral luminescence $L(v) = \frac{c \cdot \rho(v)}{4\pi}$ is Watt per m² per sr
- Spectral luminescence as a function $L(v) = \frac{2hv^3}{c^2} \left(\frac{1}{e^{\frac{hv}{k_BT}} 1}\right)$
- Spectral luminescence as a function $L(\lambda) = \frac{2hc^2}{\lambda^5} \left(\frac{1}{e^{\frac{hc}{\lambda k_BT}} 1}\right)$

Luminescent light

Common terminology for processes in which light is generated

Luminescent light

- Excitiation of system by external energy source
 - Cathodoluminescence: accelerated electrons e.g. old fashioned TV screen (CRT) – northern lights (auroras)
 - photoluminescence: optical photons e.g. White T-shirt illuminated by UV light, white LEDs
 - Chemiluminescence: chemical reaction e.g. Oxidizing phosphor
 - Bioluminescence: biochemical reaction e.g. Fireflies
 - Electroluminescence: an external electrical field e.g. LED
 - Sonoluminescence: under the influence of sound, shock wave



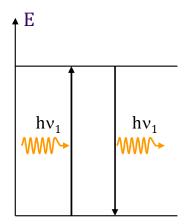
21" TV CRT Display

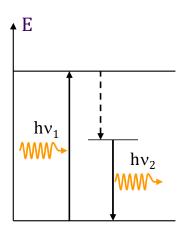


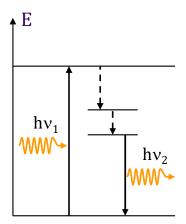


Photoluminescence

- Atomic system is excited by a photon
- Falls back to ground state by emitting a photon
- Intermediate (non-radiative) transitions possible







Fluorescence and phosphorescence

- Fluorescence:
 Singlet-Singlet transition
 = easy
- Phosphorescence:Triplet-Singlet overgang= 'not allowed'
- Singlet: as many spin-up as spin-down electrons
- Triplet: Two electrons more spin-down than spin-up or vice versa
- Ground state= Singlet

